

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
25 September 2003 (25.09.2003)

PCT

(10) International Publication Number
WO 03/078160 A1

(51) International Patent Classification⁷: **B32B 17/10**,
C08J 5/18, C08L 29/14, C08K 5/00, B64C 1/14, B29C
47/00

(21) International Application Number: PCT/US03/07353

(22) International Filing Date: 11 March 2003 (11.03.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/363,908 12 March 2002 (12.03.2002) US

(71) Applicant (for all designated States except US): **E.I. DU PONT DE NEMOURS AND COMPANY** [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **WONG, Bert, C.** [US/US]; 212 Hawkes Court, Hockessin, DE 19707 (US). **RYMER, Donald, L.** [US/US]; 4233 School House Road, Little Hocking, OH 45742 (US). **READ, Nolan, K., III** [US/US]; 2 Chadwick Square, Vienna, WV 26105 (US).

(74) Agent: **DOBSON, Kevin, S.**; **E.I. DUPONT DE NEMOURS AND COMPANY, LEGAL PATENT RECORDS CENTER**, 4417 Lancaster Pike, WILMINGTON, DE 19805 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KB, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 03/078160 A1

(54) Title: **LOW-COLOR STIFF PVB LAMINATES FOR USE IN AIRCRAFT WINDSCREENS**

(57) Abstract: The present invention describes laminate articles comprising a stiff, low-color PVB resin having a YTD of less than 12 and having a low concentration of plasticizer in the resin composition, wherein the resin is prepared from a composition that includes a PVB bleaching compound. The laminate articles of the present invention have high curvature. A laminate of the present invention can be particularly useful for aircraft windscreen applications.

TITLE
LOW-COLOR STIFF PVB LAMINATES FOR USE IN AIRCRAFT
WINDSCREENS

5 This application claims the benefit of U.S.
Provisional Application No. 60/363,908, filed March 12,
2002.

BACKGROUND OF THE INVENTION

10 Plasticized polyvinyl butyral sheet (PVB) is used
in the manufacture of laminate structures such as, for
example: windshields for vehicles including
automobiles, motorcycles, and boats; homes and
buildings; shelving in cabinets and display cases; and
15 other articles where structural strength is desirable
in a glass sheet. In many applications, it is
desirable that the laminate be transparent and
colorless, or at least have very low color. Undesired
or unintended color in a glass laminate can be a result
20 of impurities from various sources. In some cases,
color can occur in the PVB interlayer. Color in a PVB
sheet can result from several sources in the PVB resin,
or from the manufacturing process. For example, color
can result from instability of the PVB resin, from
25 impurities, or from other additives present in the PVB
composition. Color in a PVB sheet can develop during
storage of the PVB, or be caused by process conditions
to which the resin is subjected.

PVB can be manufactured according to known
30 processes. For example, U.S. Patent Number 3,153,009
describes a process for commercial manufacture of PVB.
U.S. Patent Number 4,696,971 also describes a process
for manufacturing PVB wherein sodium
dioctylsulfosuccinate (DOSS) is used as a surfactant.
35 With some exceptions that will be obvious to one
skilled in the art, the teachings of the above-

referenced patents are hereby incorporated by reference.

In a conventional PVB sheet manufacturing process, additives are typically included to protect PVB from developing color. Examples of such additives are antioxidants and light stabilizers. Light stabilizers include compounds that are capable of absorbing ultraviolet (UV) light and/or infrared (IR) light, thereby protecting the resin from the effects of this radiation. In some commercial applications, it has been found that combinations of UV light stabilizers can be required for satisfactory results. For example, conventional PVB resin compositions can include, for example, Tinuvin® 123 in addition to Tinuvin® 326 to obtain satisfactory light stability in the resin. However, using combinations of light stabilizers can add additional expense and complexity to the manufacturing process.

Conventional PVB resin sheet compositions can also require antioxidants to prevent oxidation of components in the PVB that are subject to oxidation, and can contribute to the color of the resin in an the oxidized state. For example, octylphenol can be used in combination with light stabilizers to give a PVB sheet with acceptable color and color stability. However, the effectiveness of antioxidants and light stabilizers can be dependent upon the composition of the PVB composition. Changing the PVB composition can make the antioxidant and light stabilizer ineffective in preventing the formation of color-bodies.

Conventional PVB sheet typically includes a plasticizer in order to increase the flexibility and processibility of the PVB resin. Generally, the higher the concentration of plasticizer, the more flexible the sheet. Various plasticizers are conventional in the manufacture of PVB, and include such plasticizers as:

diesters of polyethylene glycols such as triethylene glycol di(2-ethylhexanoate) (3G0) and tetraethylene glycol diheptanoate (4G7), for example. Typically, plasticizer is included in amounts of greater than 30 pph, based on the total weight of the resin. Depending upon the application, as well as other factors, highly plasticized PVB typically can have as much as 60 pph of plasticizer.

In some special applications, however, it can be desirable to include small amounts of plasticizer so that a stiff PVB resin sheet can be obtained. One problem with using low plasticizer concentrations is that the PVB composition may require exposure to higher temperatures in order to extrude the resin and/or to shape the extruded resin sheet for use in the application for which it was intended. However, when a conventional PVB resin is exposed to such high temperature, color can develop in the resin thereby making it unusable in applications where clarity and high laminate transparency are critical.

It can be desirable in the art of manufacturing PVB sheet, to have a process for making a low color PVB resin having a low concentration of plasticizer whereby the PVB composition would not develop a high color level upon exposure to high process temperatures.

It can also be desirable to have a process whereby the color of a PVB resin can be improved by proper selection of additives used in a process for manufacturing PVB.

SUMMARY OF THE INVENTION

In one embodiment, the present invention is a small laminate article having high curvature comprising a plasticized PVB resin interlayer wherein the PVB resin consists essentially of: polyvinylbutyral having a hydroxyl number of from about 15 to about 25; a

plasticizer or plasticizer mixture present in a finite amount of less than about 30 pph based on the dry weight of the resin composition; a surfactant; and optionally including either (i) a PVB bleaching
5 compound, or (ii) an antioxidant, or (iii) both (i) and (ii), wherein the interlayer was obtained after extrusion at a temperature in the range of from about 225°C to about 245°C, and wherein the interlayer has a yellowness index (YID) color of less than about 12.

10 In another embodiment, the present invention is an aircraft windscreen comprising a plasticized PVB resin interlayer wherein the PVB resin consists essentially of: polyvinylbutyral having a hydroxyl number of from about 15 to about 25; a plasticizer or plasticizer
15 mixture present in a finite amount of less than about 30 pph based on the dry weight of the resin composition; a surfactant; and optionally including either (i) a PVB bleaching compound, or (ii) an antioxidant, or (iii) both (i) and (ii), wherein the
20 interlayer was obtained after extrusion at a temperature in the range of from about 225°C to about 245°C, and wherein the interlayer has a yellowness index (YID) color of less than about 12.

25 DETAILED DESCRIPTION

In one embodiment, the present invention is small laminate article having high curvature comprising a plasticized PVB resin interlayer wherein the PVB resin consists essentially of: polyvinylbutyral having a
30 hydroxyl number of from about 15 to about 25; a plasticizer or plasticizer mixture present in a finite amount of less than about 30 pph based on the dry weight of the resin composition; a surfactant; and optionally including either (i) a PVB bleaching
35 compound, or (ii) an antioxidant, or (iii) both (i) and (ii), wherein the interlayer was obtained after

extrusion at a temperature in the range of from about 225°C to about 245°C, and wherein the interlayer has a yellowness index (YID) color of less than about 12.

PVB can be manufactured according to known processes. For example, U.S. Patent Number 3,153,009 describes a process for commercial manufacture of PVB. U.S. Patent Number 4,696,971 also describes a process for manufacturing PVB wherein sodium dioctylsulfosuccinate (DOSS) is used as a surfactant. With some exceptions that will be obvious to one skilled in the art, the teachings of the above-referenced patents are hereby incorporated by reference.

The PVB resin composition of the present invention includes the plasticizer in a finite amount, but at a concentration of less than 30 pph, based on the dry weight of the PVB resin composition. The present invention preferably includes plasticizer in an amount of from about 5 to about 30 pph, more preferably the plasticizer content is from about 15 to about 30 pph. Even more preferably the plasticizer content is from about 18 to about 28 pph, and most preferably from about 18 to about 22 pph.

The term flake, as used in the present invention, describes a particular physical form of PVB resin material, that is, granular or particulate versus a film or a sheet. The physical form of the resin does not necessarily indicate a different PVB composition within the present application, even though sheets and/or films may include additives not found in the resin flake.

Plasticizers of the present invention can be chosen from any that are known or used conventionally in the manufacture of plasticized PVB sheeting compositions. For example, a plasticizer suitable for use herein can be a plasticizer or a mixture of

amount of from about 0.15 to about 0.70 pph. While color reduction in a PVB sheet is an important consideration, the amount of bleaching compound included will also be a function of the cost of production and the other properties that may be affected by including the additive.

The present invention includes a surfactant. A surfactant suitable for use herein can be any that is known to be useful in the art of polyvinylbutyral manufacture. For example, surfactants suitable for use herein include: sodium lauryl sulfate; ammonium lauryl sulfate; sodium dioctyl sulfosuccinate; ammonium perfluorocarboxylates having from 6 to 12 carbon atoms; sodium aryl sulfonates, adducts of chlorinated cyclopentadiene and maleic anhydride; partially neutralized polymethacrylic acid; alkylaryl sulfonates; sodium N-oleyl-N-methyl taurate; sodium alkylaryl polyether sulfonates; triethanolamine lauryl sulfate; diethyl dicyclohexyl ammonium lauryl sulfate; sodium secondary-alkyl sulfates; sulfated fatty acid esters; sulfated aryl alcohols; and the like. Preferable surfactants include sodium lauryl sulfate, sodium dioctyl sulfocuccinate, sodium cocomethyl tauride, and decyl(sulfophenoxy)benzenesulfonic acid disodium salt.

The surfactant can be included in any effective amount for the particular set of process conditions practiced. The surfactant can be included in an amount of from about 0.01 to about 0.85 pph by weight, based on the weight of PVA used to prepare PVB. Preferably the surfactant is included in an amount of from about 0.10 to about 0.80 pph. More preferably, the surfactant is included in an amount of from about 0.15 to about 0.75 pph. Most preferably, the surfactant is included in an amount of from about 0.15 to about 0.70 pph.

plasticizers selected from the group consisting of:
diesters obtained from the chemical reaction of
aliphatic diols with carboxylic acids, including
diesters of polyether diols or polyether polyols; and,
5 esters obtained from polyvalent carboxylic acids and
aliphatic alcohols. For convenience, when describing
the sheet compositions of the present invention, a
mixture of plasticizers can be referred to herein as
"plasticizer". That is, the singular form of the word
10 "plasticizer" as used herein can represent the use of
either one plasticizer or the use of a mixture of two
or more plasticizers in a given sheet composition. The
intended use will be apparent to a reader skilled in
the art. Preferred plasticizers for use herein are
15 diesters obtained by the reaction of triethylene glycol
or tetraethylene glycol with aliphatic carboxylic acids
having from 6 to 10 carbon atoms; and diesters obtained
from the reaction of sebacic acid with aliphatic
alcohols having from 1 to 18 carbon atoms. More
20 preferably the plasticizer is either 4G7, 3GO or
dibutyl sebacate (DBS). Most preferably the
plasticizer is 3GO.

The composition of the present invention
optionally includes at least one PVB bleaching
25 compound. A PVB bleaching compound (bleaching
compound) of the present invention is any compound that
can reduce or eliminate color from a PVB sheet relative
to the color of an otherwise identical composition,
treated using an identical or similar process, with the
30 exception that a bleaching compound is not present.
The mode of the bleaching action demonstrated by the
bleaching compound is not critical to the present
invention. For example, a bleaching compound useful in
the practice of the present invention can be a compound
35 that reacts directly with color-forming compounds
(color bodies) present in a PVB sheet composition, or a

The surfactant and the bleaching compound can be the same compound, or can perform both functions. The bleaching compound is optional only in the event that the surfactant can also perform the function of a bleaching compound. Otherwise the bleaching compound is considered to be essential in the practice of the present invention. For example, DOSS can be used in the practice of the present invention as a surfactant. DOSS can also be a bleaching compound in the practice of the present invention. In one particularly preferred embodiment, DOSS can be included as both a surfactant and as a bleaching compound. In this embodiment, the use of a bleaching compound other than DOSS is optional.

Antioxidants can be optionally included in a PVB composition of the present invention during sheet preparation to inhibit the oxidation of the PVB sheet and/or components. Preferred antioxidants are known conventionally and available commercially. Most preferred are bis-phenolic antioxidants, which are surprisingly more suitable for preparing low color PVB sheeting, particularly when 3GO is used as plasticizer. Bis-phenolic antioxidants are available and can be obtained commercially. Suitable bis-phenolic antioxidants include 2,2'-ethylidenebis(4,6-di-t-butylphenol); 4,4'-butylidenebis(2-t-butyl-5-methylphenol); 2,2'-isobutylidenebis(4,6-dimethylphenol); and 2,2'-methylenebis(6-t-butyl-4-methylphenol), for example. Bis-phenolic antioxidants are commercially available under the tradename of ANOX™ 29, LOWINOX® 22M46, LOWINOX® 44B25, and LOWINOX® 22IB46, for example.

An antioxidant can be included in any effective finite amount. Preferably, the antioxidant is included in an amount of from about 0.01 to about 0.6%, based on the total weight of the sheet. More preferably, the

antioxidant is present in amount of from about 0.03 to about 0.3%, most preferably in an amount of from about 0.05 to about 0.25%.

Other additives are known conventionally to be useful, and can be included in a sheet composition of the present invention. Such additives include: light stabilizers, particularly UV light stabilizers, such as Tinuvin® P; Tinuvin® 326, and Tinuvin® 123. UV light stabilizers can stabilize the PVB composition by absorbing ultraviolet light and preventing unwanted effects by the UV light on the PVB. Adhesion control agents such as alkali and alkaline earth metal salts of carboxylic acids, alkaline earth metal salts of inorganic acids, or a combination of such salts can be added. Surface tension controlling agents such as Trans® 290 or Trans® 296 available from Trans-Chemco; or Q-23183A® available from Dow Chemical can be used in the practice of the present invention. The use Trans® 290 or Trans® 296 is preferred.

A PVB resin of the present invention can be obtained by processes known in the art of PVB manufacture. PVB resins used in the practice of the present invention can be prepared by mixing PVA with butyraldehyde in an aqueous medium in the presence of an acid or mixture of acids, at a temperature of from 5°C to 100°C.

Typically, the ratio of PVA to butyraldehyde can be chosen such that the PVB has residual hydroxyl functionality, conventionally reported as OH number. Residual hydroxyl functionality can vary according to what properties are desirable in the PVB. The relative amounts of butyraldehyde and PVA required to obtain the desired OH number in the PVB resin will be readily apparent to those skilled in the art of PVB manufacture. In the practice of the present invention residual hydroxyl can be in the range of from about 14

to about 30. Preferably, the OH number is from about 15 to about 25. More preferably, the OH number is from about 15 to about 20, and most preferred in the practice of the present invention is PVB resin having
5 an OH number in the range of from about 17 to about 19. The OH number can be determined according to standard methods such as ASTM D1396-92.

In a preferred embodiment, a low color PVB sheet of the present invention can be obtained by a process
10 comprising the steps: (I) admixing polyvinyl alcohol, butyraldehyde, an acid or mixture of acids, water, and a surfactant (II) stabilizing the mixture obtained in step (I) by (a) raising the pH of the mixture to at least pH 10 (b) isolating the resin by draining the
15 liquid, (c) washing the resin with neutral pH water; (III) plasticizing the PVB resin composition with from about 10 to about 30 pph of plasticizer based on the dry weight of the PVB resin; (IV) optionally mixing (a) a PVB bleaching compound and/or (b) an antioxidant and
20 a UV light stabilizer with the PVB resin composition; and (V) extruding the PVB sheet composition at a temperature of from about 225°C to about 245°C to obtain a PVB sheet having a T_g in the range of from about 35°C to about 60°C, and a YID of less than about
25 12.

The steps of the process described herein can be carried out in varied order. For example, while it can be necessary to carry out step (I) before step (II) it is not essential, for the purpose of obtaining a low
30 color sheet of the present invention, that steps (III) or (IV) be carried out in any particular order. Although it may be preferable to implement these steps just prior to, or simultaneous with, step (V). Also, the order of addition of components is not critical in
35 the practice of the present invention, although a skilled artisan will recognize that there may be other

benefits of carrying out the process in a consistent and ordered manner. For example, plasticizer can be mixed with the PVB either before or during the extrusion of the PVB composition, as described in U.S.

5 Pat. No. 5,886,075.

Plasticizer can be added in any amount desirable to obtain a plasticized PVB composition. To obtain a stiff PVB sheet in one embodiment of the present invention, plasticizer is added in an amount of less
10 than about 30 pph, based upon the total dry weight of the resin. The "dry weight" as used herein refers to the weight of the resin after water has been removed from the resin.

The glass transition temperature (T_g) of a PVB
15 sheet is dependent in part upon the concentration of plasticizer included in the composition. A PVB sheet useful in the practice of the present invention has a T_g of from about 35°C to about 60°C, as measured by Dynamic Mechanical Analysis ASTM D4065 (DMA), using the
20 tangent delta (phase shift at 1 Hz) data as indicator. Preferably, the T_g is from about 40°C to about 57°C, more preferably from about 45°C to about 57°C, most preferably from about 50°C to about 55°C.

In one of the preferred embodiments of the present
25 invention, a stiff PVB sheet can be obtained having low color and low concentration of plasticizer. For sheet having low concentration of plasticizer, it can be necessary to extrude the sheet at a higher temperature than when using higher amounts of plasticizer. For
30 example, PVB resin plasticized with from about 5 to about 30 pph plasticizer can be extruded at a temperature of from about 225°C to about 245°C. Preferably the resin can be extruded at a temperature of from about 227°C to about 245°C. More preferably,
35 the resin can be extruded at a temperature of from

about 228 °C to about 242°C, and most preferably from about 230°C to about 240°C.

A low color PVB sheet suitable for the purposes herein can be obtained by a process that comprises the steps of: (1) isolating PVB flake from a PVA/butyraldehyde reaction mixture previously described herein; (2) optionally admixing an antioxidant and a UV light stabilizer with the plasticizer to obtain a plasticizer/additive mixture (plasticizer mixture); and (3) co-extruding the flake, plasticizer, antioxidant, and UV light stabilizer, or alternatively co-extruding the flake and the plasticizer mixture at a feed ratio of plasticizer mixture to dry of flake from about 5:100 (wt:wt) to about 30:100 (wt:wt) at a temperature of from about 225°C to about 245°C to obtain a low-color PVB sheet having a YID of less than about 12. It is preferable to admix the antioxidant/UV light stabilizer with the plasticizer prior to extrusion of the sheet.

Laminates of the present invention can be useful as specialty glass laminates, such as on aircraft. Toughness, transparency and clarity are important considerations in applications such as these. Just as important is the protection afforded by the interlayer against splintering and expulsion of glass particles in the event of accidental or intentional impact against the glass laminate.

A laminate of the present invention can be obtained by a process comprising the steps of: putting together at least one layer of curved specialty glass with at least one layer of PVB of the present invention to make a glass/PVB assembly; placing the assembly into a bag capable of sustaining a vacuum; drawing air out of the bag using a vacuum line or other means of pulling a vacuum on the bag; sealing the bag while maintaining the vacuum; placing the sealed bag in an autoclave at a temperature of from about 130°C to about

180°, at a pressure of from about 200 psi (15 Bars),
for from about 10 to about 50 minutes. Preferably the
bag is autoclaved at a temperature of from about 140°C
to about 160°C for 20 minutes to about 45 minutes, more
5 preferably at a temperature of from about 145 to about
160°C for about 20 to 40 minutes, and most preferably
at about 145°C to about 155°C for about 25 to about 35
minutes.

The aircraft glass prior to lamination can have
10 functionality embedded in the glass or on the surface
of the glass. For example the glass can have various
antennae or sensors embedded in the glass or on the
surface of the glass. Such specialty glass is known or
can be obtained commercially. In any event, the
15 presence of said functionality does not add to nor
detract from the novelty of the presently claimed
invention.

The aircraft glass of suitable for use herein can
have a high curvature. Lamination of the PVB of the
20 present invention to glass having high curvature can
require lamination conditions described herein. The
curved glass can have a curvature of from about 0.1
milliradian to about 3.2 radians with a radius of
curvature of from about 20 cm to about 350 cm.

25 Laminates of the present invention can include an
additive to block the transmission of UV light through
the laminate. The additive is preferably the same
additive as the UV light stabilizer. UV light is
preferably absorbed by the laminate so that less than
30 10% of UV light is transmitted through the laminate.
Preferably less than 8% of the UV light is transmitted
through the laminate, more preferably less than 6% UV
light is transmitted, and most preferably less than 3%.

PVB interlayers of the present invention have a
35 thickness of greater than 0.254 mm. Preferably, PVB
interlayers of the present invention have a thickness

in the range of from about 0.254 mm to about 1.6 mm. Multiple layers of PVB can be laminated together or in alternate layers of a laminate. Such multilayer laminates can have PVB interlayers that have a total thickness of greater than 1 mm. Where it is desirable to obtain a laminate wherein the total interlayer thickness is at least 1 mm thick, the YID of the interlayer should not be greater than 12, because the transparency of the laminate can be substantially reduced.

EXAMPLES

The following Examples and comparative examples are presented to further illustrate the present invention. The Examples are not intended to limit the scope of the invention in any manner, nor should they be used to define the claims or specification in any manner that is inconsistent with the invention as claimed and/or as described herein.

Analytical tests for Hydroxyl number and YID were performed for each of the examples and comparative examples according to the methods below.

Hydroxyl number: ASTM D 1396-92.

25

Sheet yellowness index (YID)

A PVB chip is made with 21.0 grams of sheet, and heat pressed into a 10.0 mm thick disk of 50.8 mm diameter. Chip preparation involves preheating a stack of 50.8 mm disks cut from the sheet in a mold for one minute at 2200 N force and 185°C, then increasing the pressing force to 32,000 N at 185°C for two minutes, and cooling under the same force for 7.5 minutes. No residual surface pattern that was on the extruded sheet is visible in the chip. Yellowness index was determined per ASTM D1925-70 on the 10.0 mm thick chip.

Glass Transition Temperature - T_g is determined by DMA using the procedure of ASTM D4065, using the tangent delta at 1Hz.

Example 1

Poly(vinyl butyral) sheet was prepared as follows:
at 90°C, a mixture comprising 32 parts by weight of
poly(vinyl alcohol) of average degree of polymerization
5 618 and 99.5% hydrolyzed and 68 parts by weight of PVA
of average degree of polymerization 1005 and 99.5%
hydrolyzed was dissolved in 615 parts by weight of
demineralized water. To this solution was added 1 part
by weight of 88% para-toluene sulfonic acid and enough
10 sulfuric acid to bring the dissolved PVA solution to a
pH of 2. Using the procedure described in US Patent
3,153,009, 62 parts by weight of n-butyraldehyde and
0.47 parts by weight of 70% DOSS and the PVA solution
were charged into a vessel maintained at 90°C. After a
15 one hour hold time, a slurry was obtained and the
slurry was stabilized with a sodium hydroxide solution
to raise the pH to 11. Concurrent with the
stabilization, 0.07 parts by weight Trans[®] 290 surface
tension stabilizing agent was added. The slurry was
20 then washed and cooled with demineralized water. A
granular, white PVB resin with residual hydroxyl number
of 18.6 was obtained. The flake was mixed with 3GO
plasticizer containing 4 grams per liter of Tinuvin[®] P
and 8 grams per liter of Lowinox[®] 44B25 antioxidant and
25 was extruded so that the residence time in the
extrusion system was about 15 to 25 minutes. The feed
rate ratio of plasticizer to dry flake was 35:100
(wt:wt). Potassium formate solution was injected so as
to deliver a potassium concentration of 10 parts per
30 million (ppm) in the sheet. Melt temperature measured
at the slot die was between 210 and 215°C. Sheet YID
was 5.85.

Example 2

PVB sheet was made in the manner as in Example 1, except that the feed ratio of the plasticizer to dry PVB flake was 20:100, and the melt residence time was 25 to 40 minutes. Melt temperature at the die was 233°C. Sheet yellowness index was 5.05.

Example 3

PVB sheeting was made in the same manner as in Example 2, except that the surface pattern due to melt fracture was quenched in a water bath as disclosed in U.S. Patent 5,886,075 by Keene et al. Melt temperature was between 225°C and 230°C. Sheeting YID was 4.80, and washboard-shape pattern was clearly visible on the surface of the sheeting.

Comparative Example C1

PVB flake was prepared as in Example 1 except that 0.4 parts by weight of sodium lauryl sulfate, based on PVA, was used in the place of dioctyl sodium sulfosuccinate as the surfactant in the PVB preparation step, and no other surface tension modifiers were added. A granular, white PVB resin with residual hydroxyl number of 18.6 was obtained. Using the flake made with sodium lauryl sulfate as described here, sheet was prepared as in Example 1, except that the feed ratio of plasticizer to dry flake was 35:100. Melt temperature measured at the slot die was between 210 and 213°C. Sheet yellowness was 25.05.

Comparative Example C2

The flake described in Example C1 was used to prepare sheet as in Example 1, except that the feed rate ratio of 3GO plasticizer to dry resin of 24:100, and the potassium level in the sheet was 50 ppm, and the melt residence time in the system was 25-40 minutes. Melt temperature at the die was between 228 and 233°C. Sheet yellowness was 53.82.

WHAT IS CLAIMED IS:

1. A small laminate article having high curvature comprising a plasticized PVB resin interlayer wherein the PVB resin consists essentially of:
5 polyvinylbutyral having a hydroxyl number of from about 15 to about 25; a plasticizer or plasticizer mixture present in a finite amount of less than about 30 pph based on the dry weight of the resin composition; a surfactant; and optionally including either (i) a PVB
10 bleaching compound, or (ii) an antioxidant, or (iii) both (i) and (ii), wherein the interlayer was obtained after extrusion at a temperature in the range of from about 225°C to about 245°C, and wherein the interlayer has a yellowness index (YID) color of less than about
15 12.
2. The article of Claim 1 wherein the surfactant is DOSS.
- 20 3. The article of Claim 1 wherein the PVB resin includes a bleaching compound.
4. The article of Claim 3 wherein the bleaching
25 compound is DOSS.
5. The article of Claim 4 wherein the article is a laminate comprising at least one layer of PVB and at least one layer of glass wherein the PVB layer has a thickness in the range of from about 0.254 mm to about
30 1.6 mm.
6. The article of Claim 5 wherein the laminate comprises more than one PVB interlayer, and wherein the combined thickness of the PVB interlayers is in the
35 range of from about 0.75 to about 1.6 mm.

7. The article of Claim 5 wherein the laminate is useful as aircraft glass.

8. The article of Claim 5 wherein the laminate
5 is obtained by a process comprising the steps of: (i) putting together at least one layer of curved specialty glass with at least one layer of PVB of the present invention to make a glass/PVB assembly; (ii) placing the assembly into a bag capable of sustaining a vacuum;
10 (iii) drawing air out of the bag using a vacuum line or other means of pulling a vacuum on the bag; (iv) sealing the bag while maintaining the vacuum; (v) placing the sealed bag in an autoclave at a temperature of from about 130°C to about 180°, at a pressure of
15 from about 200 psi (15 Bars), for from about 10 to about 50 minutes.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/07353

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 B32B17/10 C08J5/18 C08L29/14 C08K5/00 C08K5/10
 B64C1/14 B29C47/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 B32B C08J C08K B64C B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 102 502 A (HOECHST AG) 14 March 1984 (1984-03-14) page 1, line 26 -page 3, line 17 page 5, line 18-26 page 6, line 16-21 examples 1,2	1,3,5-7
Y	EP 0 635 538 A (HOECHST AG) 25 January 1995 (1995-01-25) page 2, column 1, line 1-58 page 3, column 3, line 55 -column 4, line 46 page 4, column 5, line 16 -column 6, line 26; claim 8	1,3,5-7
A	US 5 187 217 A (DEGEILH ROBERT ET AL) 16 February 1993 (1993-02-16) column 1, line 35 -column 2, line 30 -/-	1,2,4

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

& document member of the same patent family

Date of the actual completion of the international search

3 July 2003

Date of mailing of the international search report

11/07/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax (+31-70) 340-3016

Authorized officer

Lindner, T

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/07353

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 696 971 A (DEGEILH ROBERT) 29 September 1987 (1987-09-29) cited in the application column 2, line 15-53 -----	1,2,4
A	EP 0 185 796 A (MITSUBISHI MONSANTO CHEM) 2 July 1986 (1986-07-02) page 1, line 2-11 page 17, line 3-24 -----	1,8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/07353

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0102502	A	14-03-1984	DE 3228076 A1	02-02-1984
			AU 1736383 A	02-02-1984
			BR 8304005 A	07-03-1984
			EP 0102502 A1	14-03-1984
			JP 59038251 A	02-03-1984
			ZA 8305480 A	25-04-1984
EP 0635538	A	25-01-1995	DE 4324167 A1	26-01-1995
			CZ 9401741 A3	15-02-1995
			EP 0635538 A2	25-01-1995
			JP 7149988 A	13-06-1995
			US 5573842 A	12-11-1996
US 5187217	A	16-02-1993	FR 2613370 A1	07-10-1988
			DE 3850803 D1	01-09-1994
			DE 3850803 T2	16-02-1995
			EP 0287416 A1	19-10-1988
			JP 1993187 C	22-11-1995
			JP 7025812 B	22-03-1995
			JP 64000104 A	05-01-1989
US 4696971	A	29-09-1987	FR 2547589 A1	21-12-1984
			AT 31193 T	15-12-1987
			BR 8402821 A	21-05-1985
			CA 1245397 A1	22-11-1988
			DE 3467896 D1	14-01-1988
			EP 0130872 A1	09-01-1985
			ES 8503692 A1	16-06-1985
			JP 1786435 C	10-09-1993
			JP 4073445 B	20-11-1992
			JP 60042402 A	06-03-1985
EP 0185796	A	02-07-1986	EP 0185796 A1	02-07-1986